

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IB 99/03281

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/94 F01N3/02 F01N3/08 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y ✓	EP 0 758 713 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 19 February 1997 (1997-02-19) cited in the application the whole document ---	1-5, 7, 9, 11, 16-20
Y ✓	EP 0 849 441 A (DR. ING. H.C. F. PORSCHE AKTIENGESELLSCHAFT) 24 June 1998 (1998-06-24) column 1, line 19 -column 4, line 55 ---	1-5, 7, 9, 11, 16-20
Y ✓	EP 0 839 996 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 6 May 1998 (1998-05-06) column 4, line 4 -column 10, line 32 ---	1-3, 5, 7, 16-20
A ✓	EP 0 862 941 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 9 September 1998 (1998-09-09) column 5, line 25 -column 21, line 3 --- -/--	1, 2, 7, 16-20



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 November 1999

Date of mailing of the international search report

29/11/1999

Name and mailing address of the ISA

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Doolan, G

INTERNATIONAL SEARCH REPORT

International Application No

GB 99/03281

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A ✓	EP 0 628 706 A (INCO LIMITED) 14 December 1994 (1994-12-14) page 2, line 50 -page 4, line 1; claim 1 -----	1,9,10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 99/03281

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 758713	A	19-02-1997	JP 9053442 A	25-02-1997
			US 5746989 A	05-05-1998
EP 849441	A	24-06-1998	DE 19653756 A	25-06-1998
			JP 10231719 A	02-09-1998
EP 839996	A	06-05-1998	JP 10141051 A	26-05-1998
EP 862941	A	09-09-1998	JP 10306717 A	17-11-1998
EP 628706	A	14-12-1994	CA 2125455 A	11-12-1994
			JP 2574132 B	22-01-1997
			JP 7096145 A	11-04-1995
			US 5422085 A	06-06-1995

PCT

M.H

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference AA 1433 PCT	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 99/ 03281	International filing date (day/month/year) 04/10/1999	(Earliest) Priority Date (day/month/year) 12/10/1998
Applicant JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the title,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

PROCESS AND APPARATUS FOR TREATING COMBUSTION EXHAUST GAS

5. With regard to the abstract,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.

1



None of the figures.

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

WISHART, I.
JOHNSON MATTHEY TECHNOLOGY CENTRE
Blounts Court
Sonning Common
Reading RG4 9NH
GRANDE BRETAGNE

RECEIVED
19 JAN 2001

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year)

16. 01. 01

Applicant's or agent's file reference
AA 1433 PCT

IMPORTANT NOTIFICATION

International application No.
PCT/GB99/03281

International filing date (day/month/year)
04/10/1999

Priority date (day/month/year)
12/10/1998

Applicant
JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office
D-80298 Munich
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Authorized officer

Fuerbass, C

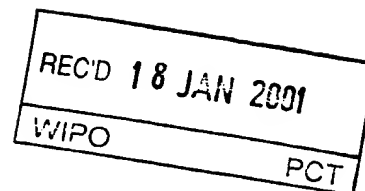
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REPLACED BY
ART 34 AMDT

PATENT COOPERATION TREATY

PCT



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AA 1433 PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/03281	International filing date (day/month/year) 04/10/1999	Priority date (day/month/year) 12/10/1998
International Patent Classification (IPC) or national classification and IPC B01D53/94		
Applicant JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 6 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 10/05/2000	Date of completion of this report 16. 01. 01
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Maremonti, M  Telephone No. +49 89 2399 8440

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/03281

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

Description, pages:

1-11 as originally filed

Claims, No.:

1-21 with telefax of 05/10/2000

Drawings, sheets:

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/03281

☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	3,5,6,9,13,15
	No:	Claims	1,2,4,7,8,10,11,12,14
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-21
Industrial applicability (IA)	Yes:	Claims	1-21
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/03281

Re Item I

Basis of the report

1. In dependent claim 4, which corresponds to claim 2, as originally filed, the feature that the compounds (a) of the NO_x absorber have to be "capable of forming nitrates and/or nitrites of adequate stability in absorbing conditions and of evolving nitrogen oxides and/or nitrogen in regenerating conditions" has been deleted. This amendment results in a broadening of the scope of claim 4, for which no basis can be found in the application as filed, contrary to the provisions of Article 34(2)b) PCT (see also p. 3, l. 23-26, where the mentioned feature is reported). As a consequence, this modification was ignored in the establishment of the present examination report (Rule 70(2)c) PCT).

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- 1.1 Reference is made to the following documents:

D1: EP-A-0 758 713 cited in the application
D2: EP-A-0 839 996
D3: EP-A-0 862 941
D4: EP-A-0 628 706

- 1.2 The present application does not meet the requirements of the PCT, because the subject-matter of independent claim 1 is not novel in the sense of Article 33(2) PCT. Indeed document D1 discloses an apparatus suitable for treating a combustion exhaust gas, comprising (cf. c. 2, l. 41-55; c. 3, l. 12-22; c. 6, l. 39-48; c. 8, l. 3-23 and Figure 1) an oxidation catalyst (5) effective to promote the conversion of NO to NO₂, a filter (7) placed downstream of said catalyst and effective to collect soot and hold it for combustion by reaction with the NO₂ in the gas, an NO_x absorber (9) charged with a regenerable solid absorbent, means (4) for introducing intermittently a regenerant of the absorber, which means is considered to be suitable for injecting a NO_x-specific reactant upstream of the absorber (cf. Figure 1); and, associated with the absorber, a catalytic system able

to oxidise HC and CO and to reduce NO_x to N₂. Therefore, D1 discloses all structural features of the apparatus defined in claim 1.

1.3 As far as independent claim 16 is concerned, it is noted that D1 also discloses a process suitable for treating a combustion exhaust gas, which process is carried out in the apparatus discussed in the previous paragraph. The process of D1 comprises steps corresponding to the above-mentioned apparatus features. The subject-matter of claim 16 differs from the process of D1 only in that an NO_x-specific reactant is intermittently introduced in order to regenerate the absorber, whereas in D1 a general reductant is injected for the same purpose, like, for example, engine fuel (cf. c. 8, l. 3-23).

1.4 Both an NO_x-specific reactant and a general reducing agent actually accomplish the same function (promotion of NO_x desorption) and in the same way (decrease of the oxidant level). As D1, also documents D2 and D3 disclose the injection of a general reducing agent for the NO_x absorber regeneration, like a general hydrocarbon, hydrogen gas or carbon monoxide (cf. D2: c. 4, l. 51-57; D3: c. 9, l. 26-31).

However, the injection of an NO_x-specific reactant in order to diminish the oxidant level is also known to a person skilled in the art in particular from document D4, which clearly reports that both a general reducing agent and a specific NO_x reactant can be added in the process disclosed therein (cf. p. 2, l. 54-57 and Figure 2). Moreover, the same NO_x-specific reactants as in the present application are revealed in D4, i.e. ammonia and urea (cf. claim 1).

Therefore, the injection of an NO_x-specific reactant, instead of a general reducing agent, in the process of D1 is merely regarded as one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill.

As a consequence, the subject-matter of claim 16 is not regarded as to involve an inventive step in the sense of Article 33(3) PCT.

2. Dependent claims 2-15 and 17-21 do not appear to contain any additional feature which, in combination with the features of any claim to which they refer, meets the requirements of the PCT with respect to novelty and inventive step (Articles 33(2) and (3) PCT). All mentioned features are, indeed, either known from D1-D4 (cf.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/03281

D1: c. 5, l. 46-58 and l. 38-43, c. 3, l. 54-55, c. 4, l. 25-32, c. 8, l. 21-23 and Figure 1; D2: c. 4, l. 51-57, c. 5, l. 33-50; D3: c. 6, l. 36-37, c. 7, l. 5-16; D4: claim 1) or they are regarded as obvious design possibilities for a person skilled in the art.

3. The subject-matter of all claims is regarded as to be industrially applicable (Articles 33(4) PCT).

Re Item VII

Certain defects in the international application

1. The units "cells per square inch" on pages 2, 7 and 8, "inches" and "g/in³" on page 8 are not SI units (Rule 10.1(a) PCT).
2. Reference signs have not been inserted in the claims, placed between parentheses, in order to facilitate quicker understanding (Rule 6.2(b) PCT).
3. In claim 15, the wording "An engine according to claim 8" should be read as "An engine according to claim 14".

Re Item VIII

Certain observations on the international application

1. In independent claim 16, the wording of step (vi) is not clear (Article 6 PCT). Particularly, the meaning of the expression "with the gas the product of step (v)" is not clear. Apparently, the gas leaving the absorbent should be intended.
2. In dependent claim 13, reference is made to an "engine" but no engine was defined in claim 12, to which claim 13 refers (Article 6 PCT).
3. Examples 1-3 reported in the description do not represent particular embodiments of the entire process as claimed in claim 16 but rather of a single step of the process, namely the regeneration step.

CLAIMS:

1. A system for treating combustion exhaust gas, which system comprising: a catalyst effective to promote oxidation of at least NO to NO₂; a filter downstream of the
5 oxidation catalyst, which filter being effective to collect soot and hold it for combustion reaction with the NO₂ in the gas; a NO_x absorber downstream of the filter, which NO_x absorber is charged with solid absorbent; means for introducing intermittently a regenerant of the absorber, which means being effective to inject a NO_x-specific reactant upstream of the absorber; and, associated with and/or downstream of the
10 absorber, a catalyst system effective to promote reactions of hydrocarbons (HC) and CO with O₂ to H₂O and CO₂ and to react NO_x to N₂.
2. A system according to claim 1, wherein the catalyst system is associated with the absorber.
- 15 3. A system according to claim 1, wherein the catalyst system is disposed in a separate bed downstream of the absorber.
4. A system according to claim 1, 2 or 3, wherein the NO_x absorbent comprises: (a)
20 compounds of alkali metals, alkaline earth metal, rare earth metals and transition metals or a mixed oxide of any two or more thereof; and/or (b) zeolites, carbons and/or high surface area oxides.
5. A system according to claim 4, wherein the mixed oxide includes Ba-Cu-O,
25 MnO₂-BaCuO₂, optionally including CeO₂, Y-Ba-Cu-O or Y-Sr-Co-O.
6. A system according to any of claims 1 to 5, wherein the catalyst system comprises vanadia/titania and/or one or more platinum group metal.
- 30 7. A system according to any of claims 1 to 6, wherein the injection means is arranged to inject the reactant upstream of the filter.
8. A system according to claim 7, wherein the injection means is arranged to inject the reactant upstream of the oxidation catalyst.

9. A system according to any of claims 1 to 6, wherein the injection means is arranged to inject the reactant downstream of the filter.
- 5 10. A system according to any preceding claim, wherein the filter is catalysed.
11. A system according to any preceding claim, wherein the injection means is for ammonia, hydrazine, urea or aqueous urea solution.
- 10 12. A system according to any preceding claim including sensors, indicators, computers and actuators, effective to maintain operation within desired conditions.
13. A system according to claim 12, wherein a computer operates the engine in compliance with the European Stage IV emission legislation.
- 15 14. A diesel engine including a system according to any preceding claim.
15. An engine according to claim 8 which is a turbo-charged direct injection engine.
- 20 16. A process for treating combustion exhaust gas containing CO, hydrocarbons (HC), NO, O₂, soot and non-reactive gases, which process comprises the steps of: (i) catalysing oxidation of NO to NO₂; (ii) collecting soot on a filter; (iii) combusting the collected soot by reaction with NO₂ and possibly also O₂ left over after step (i); removing NOx from the product of step (iii) by contacting a regenerable NOx absorbent
25 with gas containing it; (v) regenerating the absorbent intermittently by injecting a NOx-specific reactant upstream of the absorbent; and (vi) at least during step (v), contacting a catalyst system effective to promote reactions of HC and CO with O₂ to H₂O and CO₂ and to react NOx to N₂ with the gas the product of step (v).
- 30 17. A process according to claim 16, wherein the reactant is injected into: (a) lean exhaust gas as generated by the engine or the product of a preceding step of exhaust treatment; or (b) gas made leaner when the NOx-specific reactant is injected with air.

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18. A process according to claim 16 or 17, wherein the NO_x-specific reactant is ammonia or hydrazine and is injected as such and/or as a precursor compound decomposable thereto *in situ*.

5 19. A process according to claim 16, 17 or 18, wherein the precursor is urea or aqueous urea solution.

20. A process according to claim 16, 17, 18 or 19, wherein the exhaust gas is the product of combustion of fuel containing less than 50 ppm w/w of sulphur.

10

21. A process according to any of claims 16 to 20, operated in compliance with the European Stage IV emission legislation.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01D 53/94, F01N 3/02, 3/08, 3/20	A1	(11) International Publication Number: WO 00/21647 (43) International Publication Date: 20 April 2000 (20.04.00)
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(21) International Application Number: PCT/GB99/03281

(22) International Filing Date: 4 October 1999 (04.10.99)

(30) Priority Data:

9822083.3 ✓	12 October 1998 (12.10.98)	GB
9917042.5 ✓	21 July 1999 (21.07.99)	GB

(71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).

(72) Inventor; and

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(74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

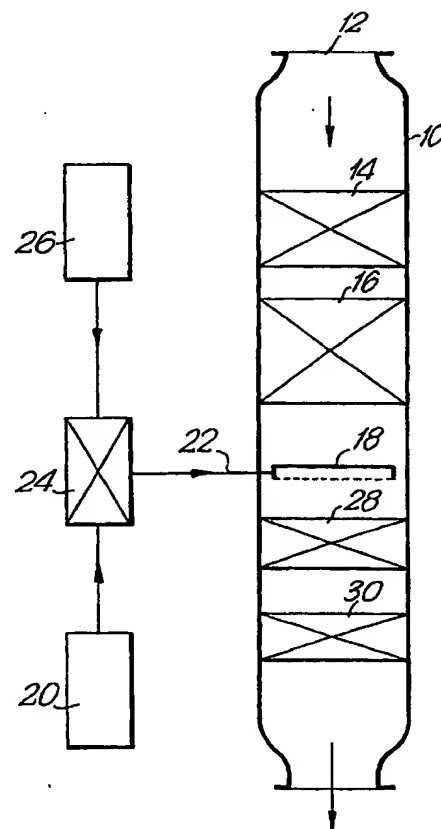
Published

With international search report.

(54) Title: PROCESS AND APPARATUS FOR TREATING COMBUSTION EXHAUST GAS

(57) Abstract

A system and method for the control of emissions from a diesel engine exhaust, comprises a catalyst (14) to convert NO to NO₂, a filter (16) to trap soot and hold it for combustion with the NO₂, and a NO_x absorber (28), with means to regenerate the NO_x absorber by injecting reductant or other reactant (injector 18) upstream of the absorber, and at least during regeneration, passing the exhaust gases leaving the absorber through a three-way catalyst (30).



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EE	Estonia						

PROCESS AND APPARATUS FOR TREATING COMBUSTION EXHAUST GAS

5

This invention concerns emission control especially for diesel engine exhaust gas.

EP-A-0341832 and corresponding US 4902487 describe a process and treatment system for removing soot from diesel exhaust gas containing NO by passing such gas
10 unfiltered over an oxidation catalyst to convert NO to NO₂, collecting the soot on a filter and using the resulting gas containing NO₂ to combust the collected soot, the amount of NO converted to NO₂ being sufficient to enable such combustion to proceed at a temperature less than 400C.

15 EP-A-0758713 describes a process in which such a soot combustion step is followed by removing NO_x from the combustion outlet gas by means of a solid absorbent and regenerating the absorbent by intermittent engine fuel inlet adjustment or injection of reductant into the exhaust gas upstream of the oxidation catalyst. This process has disadvantages, for example requiring engine modification.

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According to the invention there is provided a process for treating combustion exhaust gas containing CO, HC, NO, O₂, soot and non-reactive gases, by the steps:

- i. catalysing oxidation of NO to NO₂;
- ii. collecting on a filter soot from the product of i;
- 25 iii. combusting the collected soot by reaction with NO₂ and possibly also any O₂ left over after the reactions in i;
- iv. removing NO_x from the product of iii by the action of a regenerable NO_x absorbent;
- v. regenerating the absorbent intermittently by:
 - 30 (a) decreasing the net oxidant level by injecting reductant upstream of the absorber but downstream of the oxidation catalyst; and/or
 - (b) injecting a NO_x-specific reactant upstream of the absorbent; and
- vi. at least during said regeneration, subjecting the gas leaving the absorbent to a catalyst system effective to promote reactions of HC and CO with O₂ to H₂O and
35 CO₂ and of NO_x to N₂.

The invention provides a treatment system for such exhaust gas comprising catalysts and absorbent corresponding to the process steps, in particular, in combination and in order: a catalyst effective to promote oxidation of at least NO to NO₂; a filter effective to collect the soot and hold it for combustion reaction with the NO₂ in the gas; a NO_x absorber charged with solid absorbent; means for introducing intermittently a regenerant of the absorber, such means being effective to introduce reductant upstream of the absorber but downstream of the oxidation catalyst; and/or to introduce a NO_x-specific reactant upstream of the absorber; and, associated with or downstream of the absorber a catalyst system effective to promote reactions of HC and CO with O₂ to H₂O and CO₂ and of NO_x to N₂.

In addition, the system may include routine features, for example means to adjust the temperature of the gas to the level required in the next downstream chemical step.

The system may be structured within a single housing ("can"), or in separated housings according to engine design and under-floor or other space considerations. Thus for example for V-engine configurations, some or all of the elements of the system may be disposed in parallel.

The catalysts and absorbent are suitably supported on a ceramic or metal honeycomb, the ceramic comprising one or more of alumina, silica, titania, cordierite, ceria, zirconia, silicon carbide or other, generally oxidic, material. The honeycomb carries a washcoat and, in one or more layers thereon, the active catalytic and/or absorptive material, to be described in more detail below. The honeycomb has typically at least 50, for example 50-400, cells per square inch, possibly more, eg up to 800, or up to 1200 if composed structurally of metal. Generally the range 200-800 is preferred for the catalysts and absorbent.

In the oxidation catalyst the active material comprises generally a platinum group metal ("PGM"), especially platinum and/or palladium, optionally with other PGMS, eg rhodium, and other catalytic or promoting components. The exact compositions and structure of the oxidation catalyst are not critical to operation of the invention, and hence may be varied according to the requirements of the situation. A low temperature light-off formulation

is generally preferred. Conventional manufacturing techniques may be used. The catalyst should of course be sized and composed to achieve the necessary conversions, and the design should minimise trapping of soot within its honeycomb.

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The filter may be any capable of trapping the soot without causing excessive back-pressure. In general, ceramic, sintered metal or woven or non-woven wire filters are usable, and wall-flow honeycomb structures may be particularly suitable. The structural material of the filter is preferably porous ceramic oxide, silicon carbide or sintered metal. A coating such as alumina, and also a catalyst such as one or more PGMs (eg Pt with MgO) or La/Cs/V₂O₅ may be present. The soot is generally carbon and/or heavy hydrocarbons, and is converted to carbon oxides and H₂O. Certain embodiments of this principle are in commercial use in Johnson Matthey's Continuously Regenerating Trap technology, and are described in the above-mentioned EP-A-0341832 and US 4902487, the teaching of which is incorporated herein by reference.

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The NO_x absorbent (referred to also as a "NO_x-trap"), to be described further below, may be provided in one unit or a succession of separate units. It may be in the form of active layers on a conventional honeycomb substrate, or may be in the form of serial deposits on a single honeycomb or possibly multiple honeycombs.

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The absorbent may be selected from:

- (a) compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals, capable of forming nitrates and/or nitrites of adequate stability in absorbing conditions and of evolving nitrogen oxides and/or nitrogen in regenerating conditions; and/or
- (b) adsorptive materials such as zeolites, carbons and high-area oxides.

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Compounds (a) may be present (before NO_x absorption) as composite oxides, eg of alkaline earth metal and copper such as Ba-Cu-O or MnO₂-BaCuO₂, possibly with added Ce oxide, or Y-Ba-Cu-O and Y-Sr-Co-O. (The oxides are referred to for simplicity, but in practice hydroxides, carbonates and nitrates are present, depending on the temperature and gas composition). Whichever compounds are used, there may be present also one or more

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catalytic agents, such as precious metals, effective to promote such reactions as the interchanges of the nitrogen oxides and the action of reductant and/or NO_x-specific reactant.

5 The catalyst system for step vi can be any that is active at the prevailing temperature and not adversely affected by exposure to lean gas between regeneration periods. It may be associated with the absorbent or may, alternatively or additionally, be in a separate bed. Typically it comprises one or more PGMs, especially Pt, Rh, Pd and combinations thereof, on a high-surface washcoat on a honeycomb structure as described above. Suitable catalysts are
10 of the '3-way' or 'SCR' type. Many others have been described in the literature and are available to skilled persons.

 If that catalyst system is associated with the absorbent, that is, the absorber is 'catalysed', the catalytic material may be for example co-precipitated or co-impregnated or co-
15 deposited with NO_x absorbent or present as one or more sandwiched layers or as fine (eg 10-500 microns) particles on or in a layer of absorbent or among particles of absorbent.

 For regeneration of the NO_x absorber:

1. as reductant, hydrocarbon may be introduced, for example gasoline or diesel fuel, which is
20 especially convenient, or another such as light oil, kerosene or a C3 to C8 paraffin;
2. as reductant, there may be injected hydrogen (suitably generated in situ on board the vehicle) or a readily dehydrogenatable reductant such as a lower alcohol, especially methanol or ethanol. If reductant is injected as specified, that is, downstream of the oxidation catalyst, introduction of the same or a different reductant upstream of the
25 oxidation catalyst, possibly by engine management, eg to provide for reaction increasing gas temperature, is not excluded, but is controlled to give gas lean enough for absorption of NO_x to continue. The intermittent reductant injection downstream of the oxidation catalyst then decreases the oxidant content to a NO_x desorption level;
3. a preferred technique comprises injecting a NO_x-specific reactant, especially a nitrogen
30 hydride for example ammonia or hydrazine. This can be injected as such or as a solution in eg water or as a precursor compound, for example urea or aqueous urea solution, producing the reactant in exhaust treatment conditions. Such compounds are referred to herein as 'ammonia' at stages after injection. Injectors for such reactants or compounds,

possibly using carrier gas such as air, have been published.

For regeneration using a NO_x-specific reactant, the oxidant level can be decreased less, if at all, than when using reductant. Indeed the reactant may be used especially in lean conditions, for example:

- (a) exhaust gas as generated by the engine or as issuing from a preceding step of exhaust treatment;
- (b) such gas to which reductant short of equivalence has been or is being added;
- (c) gas made leaner, for example when the reactant is injected with the aid of air.

Regeneration using NO_x-specific reactant is also effective in:

- (d) rich or equivalent gas and also in gas into which reductant has been introduced eg to provide for reaction increasing gas temperature but leaving the gas net-lean in composition.

The point of injection of the reactant may most simply be downstream of the filter; in this event the temperature is typically in the range 150°-300°C. However, injection may be earlier; if upstream of the filter but downstream of the oxidation catalyst, the temperature is typically in the range 250°-350°C at filter inlet, as required for soot combustion. Further, the reactant may be injected upstream of the oxidation catalyst. Since in such earlier injection the fed reactant is at a 'spike' concentration to react with NO_x to be evolved over the short period of regeneration of the absorber, it is in substantial excess over the NO_x in the flowing exhaust gas and consequently need not suffer much loss by reaction with NO_x. If in an extreme case it were to react with all the flowing NO_x to give N₂ or N₂O, this would stop combustion of soot on the filter: however, owing to the shortness of the ammonia injection spike, any accumulation of soot would be small and combustion would be resumed before blockage took place. The temperature should not be high enough to give substantial oxidation of ammonia to NO_x over the oxidation catalyst. To limit unwanted side-reactions of ammonia, it may be introduced as a precursor compound, thus delaying availability of ammonia. Such limitation may also be provided by suitable formulation of the oxidation catalyst and/or filter. In particular, the filter may be of the non-catalysed type, free of deliberately introduced catalytic material such as PGM. Any fortuitous catalytic activity of the filter, due for example to its structural material or accumulated deposits such as carbon,

appears not to seriously promote such side-reactions.

5 The rate of provision of the reactant should be as nearly as possible stoichiometric to the quantity of NO_x to be reacted. Especially when injection is to be upstream of the filter, the rate should be controlled in response to measurements of final exit NO_x and ammonia. In the process using the reactant there may also be enrichment of the gas by introduction of non-specific reductant.

10 Decrease of net oxidant level by injection of reductant between the oxidation catalyst and the filter or (preferably) between the filter and the absorbent to provide least interference with soot combustion, suitably produces a gas composition corresponding to an air/fuel weight ratio in the range 10 to equivalence.

15 Usually the regeneration phase can be a small fraction, eg 0.1% to 5%, of engine running time, depending of course on operating conditions.

The invention provides also an engine in combination with the system and a process of operating such an engine. The combination may include established expedients such as 20 electric heating, EGR, or recycle of released NO_x to one or more points upstream of the soot filter.

Control of the process and engine, in particular the means to regenerate the NO_x absorber, includes for example:

- 25 1. response to ultimate detection of NO_x or ammonia leakage from the absorber and/or final exit gas;
2. response to prediction based on input of data on deliberate or load-responsive engine management variation;
3. allowance for gas composition variations, for example non-steady conditions such as 30 incomplete warm-up or weather. In particular, injection is timed to occur when the temperature is at a level permitting regeneration.

Thus the combination may include sensors for at least one of: fuel composition; air/fuel ratio at engine inlet; exhaust gas compositions and temperatures at critical stages; pressure drop

especially over the filter. It may include also indicator means informing the engine operator, computer means effective to evaluate the data from the sensor(s), and control linkages effective to adjust the engine to desired operating conditions taking account of e g start-up, varying load and chance fluctuations.

Preferably the engine is a diesel engine, although other engines, including direct injection gasoline engines, may also benefit from the invention. The engine may be the motive power for a vehicle, or may be a stationary power source or auxiliary power source. It may be for a 'heavy duty' vehicle, ie at least 3500 Kg, or a 'light duty' vehicle, including in particular a passenger car or light van and likely to be operated according to the 'urban cycle'.

Desirably, the engine is fuelled with low-sulphur fuel, ie having less than 50ppm of sulphur, by weight as elemental S. For operation with higher sulphur fuels, a SOx absorbent may be used at some stage upstream of the NOx absorber.

The invention will be more fully understood from the following description of one preferred embodiment thereof, with reference to the accompanying drawing, which shows schematically in a single figure a system of catalysts and absorber suitable for carrying out the invention.

The system consists of single "can" 10, which is connected at 12 to the exhaust from a diesel engine (not shown) fuelled with diesel oil of under 50 ppm sulphur content. At the inlet end of can 10 is catalyst 14, which is a low temperature light-off oxidation catalyst supported on a 400 cells/in² ceramic honeycomb monolith. Catalyst 14 is designed to be capable of meeting emission regulations in relation to CO and HC for the engine and vehicle and also converts at least 70% of the NO to NO₂.

The gas leaving catalyst 14 passes into soot filter 16, which is of the ceramic wall flow type and collects particles over 50nm. The NO₂ and surplus oxygen in the gas oxidise the soot at temperatures around 250°C with no accumulation or tendency to blocking.

The gas leaving filter 16 is passed over sparging spray injector 18, from which it

may receive regenerant fluid such as liquid reductant or NOx-specific reactant such as gaseous ammonia or ammonia precursor from supply tank 20 via line 22. Injector 18 is fed by pump 24 under the control of engine management system 26. Pump 24 suitably acts in a pulse mode and feeds NOx-specific reactant at a rate stoichiometrically equivalent to the NOx to be released.

The gas from 18, possibly carrying regenerant fluid, then enters NOx absorber 28. During normal lean operation of the engine and without injection at 18, absorber 28 substantially removes all NOx flowing. When, however, gas containing injected regenerant reaches it, the NOx is released, and is converted to N₂ to an extent depending on whether absorber 28 is catalysed. The gas, if still containing regenerant, NOx and O₂, passes into 3-way catalyst 30, where these reactants are brought substantially to chemical equilibrium as non-polluting gases. If such reactions take place sufficiently over absorber 28, the gas leaving 28 is discharged to atmosphere. If a NOx-specific reagent is used as regenerant, catalyst 30 can be an SCR catalyst. Absorber 28 and catalyst 30 may be adjacent or mixed together on a single honeycomb.

The process and system of the invention is expected to be capable of meeting European Stage IV emission legislation, with all regulated emissions comfortably within the standards set.

EXAMPLE 1

NOx-Trap Regeneration with Diesel Fuel

A NOx-trap comprising a 400 cpsi monolith having wall thickness of 6/1000 of an inch, measuring 5.66 x 6 inches, carrying a coating containing barium (13.2%), platinum (1.7%), rhodium (0.17%), with minor proportions of alumina, ceria and zirconia with a total loading of 3.5 g/in³ was subjected to a CRT-treated gas stream from a 1.9 litre naturally aspirated direct injection diesel engine (Swedish MK-1 fuel) and containing NOx (260 ppm) at a catalyst inlet temperature of 310°C for 30 seconds during which time it began to become saturated with stored NOx. Upon introduction of MK-1 diesel fuel into the exhaust gas stream in front of the NOx-trap at a rate of 1 g/s for 3 seconds, the NOx-trap regenerated,

such that it was able to store NOx once more. The original operating conditions were restored whereby the same amount of NOx was stored, and this process was repeated many times without deterioration of the NOx capacity of the trap.

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EXAMPLE 2

NOx-Trap Regeneration with EGR + Fuel Injection

A NOx-trap as Example 1 was subjected to a CRT-treated gas stream containing NOx (145 ppm) at a catalyst inlet temperature of 220°C for 30 seconds during which time it stored NOx. The engine was as in Example 1, with EGR to reduce the oxygen concentration in the gas stream. MK-1 Diesel fuel was fed into the exhaust gas stream in front of the NOx-trap at a rate of 1 g/s for 1.5 seconds, to regenerate the NOx-trap; it was then able to store NOx once more. The original operating conditions were restored whereby the same amount of NOx was stored, and this process was repeated many times without deterioration of the NOx capacity of the trap.

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Analogous successful runs were performed at other temperatures between 180°C and 330°C, with fuel injection for different times.

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EXAMPLE 3

NOx-Trap Regeneration with Ammonia

(a) A NOx-trap as Example 1, but also including palladium (1.7%) was subjected to a gas stream containing NOx (100 ppm), O₂ (9.55%), CO₂ (8.2%) and H₂O (9%) at catalyst inlet temperatures from 200° to 300°C for 60 seconds during which time it began to saturate with stored NOx. Upon introduction of ammonia (500 ppm) and cutting off O₂ for 60 seconds, the NOx-trap regenerated, such that it was able to store NOx once more. Original operating conditions were restored as Example 1.

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In each of the above Examples the NOx trap outlet gas became rich during the regeneration period and was at a temperature at which a 3-way Pt/Rh catalyst would decompose NOx, HC and CO present in it.

(b) The run described in paragraph (a) was repeated but with the difference that for each temperature level the flow of gas was maintained with O₂ feed cut off and ammonia was injected only long enough to stabilise the temperature; this also fully regenerated the NO_x absorber. Then the O₂ feed was resumed, initially for 60 seconds without ammonia injection (NO_x absorption), then for 60 seconds with ammonia (regeneration); this alternation was maintained for 300 seconds.

Successive 300-second runs were carried out at stepped temperatures. The outlet NO_x contents ppm v/v were:

150°-170°C:	30-40
200°:	30
250°:	25
300°:	25 rising to 45
350°:	25 rising to 100

it is evident that at over 300°C there is considerable side reaction of ammonia to NO_x. However, at 150°-300°C absorption of NO_x and regeneration by ammonia are effective, even in the presence of O₂.

In each of the above Examples the NO_x trap outlet gas became rich during the regeneration period and was at a temperature at which a 3-way Pt/Rh catalyst would decompose NO_x, HC and CO present in it.

(c) By way of illustrating injection of ammonia upstream of the filter and use of the ammonia precursor urea, a part-system consisting of item 14 (oxidation catalyst) and item 16 (non-catalysed cordierite soot filter), was set up and equipped between 14 and 16 with a sparging spray injector fed from a reservoir of 32%w/w aqueous urea. The system included sensors for NO_x and NO at engine outlet and 16 outlet. The inlet of 14 was fed with the exhaust of a 10 litre Volvo diesel engine. NO_x levels were measured initially without urea injection, then at intervals during urea injection at approximate equivalence to the NO_x in the gas as received, then after stopping urea injection. Runs were carried out at temperatures in the range 225°-350°C. Gas analyses for 290°C may be regarded as typical, and were as follows, measured in ppm v/v:

	NOx	NO	NO ₂
Engine-out	540	505	35
16 out (no urea)	525	200	325
5 16 out (urea)	400	160	240
16 out (urea stopped)	520	350	170
*****		check 170	350

10 It is evident that injection of urea has decreased the NOx content of the gas by only
about 25%, leaving about 75% of the urea-derived ammonia available for use downstream of
filter 16. In a system in which ammonia is to regenerate a NOx absorber, the ratio of
ammonia to NOx at the inlet of 16 would be a 'spike', i e, much higher than stoichiometric
and fully enough ammonia would reach the NOx absorber. Likewise, such a spike of
15 ammonia, especially if added as urea, would sufficiently escape reaction over oxidation
catalyst 14.

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CLAIMS

1. A process for treating combustion exhaust gas containing CO, HC, NO, O₂, soot
5 and non-reactive gases, by the steps:

i. catalysing oxidation of NO to NO₂;

ii. collecting soot on a filter from the product of i;

iii. combusting the collected soot by reaction with NO₂ and possibly also O₂ left over after the
reactions in i;

10 iv. removing NO_x from the product of iii by the action of a regenerable NO_x absorbent;

v. regenerating the absorbent intermittently by:

(a) decreasing the net oxidant level by injecting reductant upstream of the absorber but
downstream of the oxidation catalyst; and/or

(b) injecting a NO_x-specific reactant upstream of said absorbent; and

15 vi. at least during said regeneration, subjecting the gas leaving the absorbent to a catalyst
system effective to promote reactions of HC and CO with O₂ to H₂O and CO₂ and to react
NO_x to N₂.

2. Process according to claim 1 in which the NO_x absorber comprises:

20 (a) compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals,
capable of forming nitrates and/or nitrites of adequate stability in absorbing conditions and of
evolving nitrogen oxides and/or nitrogen in regenerating conditions; and/or

(b) adsorptive materials such as zeolites, carbons and high-area oxides.

25 3. Process according to claim 1 or claim 2 in which in the absorber the catalyst system of step
vi is associated with the absorbent.

4. Process according to any one of the preceding claims in which the catalyst system in
step vi includes a separate bed following the absorber.

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5. Process according to any one of the preceding claims in which the catalyst
associated with or following the absorber comprises vanadia/titania and/or one or more
platinum group metals.

6. Process according to any one of the preceding claims in which reductant or reactant is introduced after step iii.

5 7. Process according to any one of the preceding claims in which the reductant is a hydrocarbon, hydrogen or dehydrogenatable organic compound.

8. Process according to claim 7 in which the air/fuel weight ratio of the exhaust gas containing injected reductant is in the range 10 to equivalence.

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9. Process according to any one of claims 1 to 6 in which the NO_x-specific reactant is ammonia or hydrazine and is injected as such and/or as a precursor compound decomposable thereto in situ.

15 10. Process according to claim 9 in which ammonia is injected as urea or aqueous urea solution.

11. Process according to claim 9 or claim 10 in which the reactant is injected into:
(a) lean exhaust gas as generated by the engine or as issuing from a preceding step of exhaust
20 treatment; or
(b) such gas to which reductant short of equivalence has been or is being added; or
(c) gas made leaner, for example when the NO_x-specific reactant is injected with the aid of air.

25 (d) rich or equivalent gas or gas into which reductant has been introduced eg to provide for reaction increasing gas temperature but leaving the gas net-lean in composition.

12. Process according to any one of claims 9 to 11 in which the reactant is injected upstream of the filter.

30 13. Process according to claim 12 in which the filter is non-catalysed.

14. Process according to claim 12 or claim 13 in which the reactant is injected upstream of the oxidation catalyst.

15. Process according to any one of the preceding claims in which the exhaust gas is the product of combustion of a fuel containing less than 50 ppm w/w of sulphur.

5 16. System for treatment of combustion exhaust gas having integers corresponding to the process according to any one of the preceding claims.

17. System according to claim 16 comprising, in combination and in order: a catalyst effective to promote oxidation of at least NO to NO₂; a filter effective to collect soot and
10 hold it for combustion reaction with the NO₂ in the gas; a NO_x absorber charged with solid absorbent; means for introducing intermittently a regenerant of the absorber, such means being effective to introduce reductant upstream of the absorber but downstream of the oxidation catalyst; and/or to introduce a NO_x-specific reactant upstream of the absorber; and, associated with and/or downstream of the absorber a catalyst system effective to promote
15 reactions of HC and CO with O₂ to H₂O and CO₂ and to react NO_x to N₂.

18. A diesel engine having a system according to claim 16 or claim 17 connected to its exhaust outlet.

20 19. An engine according to claim 18 which is of the turbo-charged direct injection type.

20. A process, system or engine according (as appropriate) to any one of the preceding claims, including sensors, indicators, computers and actuators, effective to maintain operation within desired conditions.

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21. A process, system or engine substantially as described and as illustrated by the foregoing specific description.

22. A process, system or engine according (as appropriate) to any one of the preceding
30 claims, operated in compliance with the European Stage IV emission legislation.

